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A Lithium Amide-Borohydride Solid-State Electrolyte with Lithium-Ion Conductivities Comparable to Liquid Electrolytes

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Abstract

We report high ionic conductivity of up to $6.4 \times 10^{-3} \text{ S cm}^{-1}$ near room temperature (40 °C) in lithium amide-borohydrides, comparable to values of liquid organic electrolytes commonly employed in lithium-ion batteries. We apply density functional theory coupled with X-ray diffraction, calorimetry, and nuclear magnetic resonance experiments to shed light on the conduction mechanism. An $\text{Li}_4\text{Ti}_5\text{O}_{12}$ half-cell battery incorporating the lithium amide-borohydride electrolyte exhibits good rate performance up to 3.5 mA cm^{-2} (5C) and stable cycling over 400 cycles at 1C at 40 °C, indicating high bulk and interfacial stability. Our results demonstrate the potential of lithium amide-borohydrides as solid-state electrolytes for high-power lithium-ion batteries.

1. Introduction

Recent developments of solid-state electrolytes (SSEs) for all-solid-state lithium-ion batteries have focused mainly on oxide and thiophosphate compounds. Ion conducting oxides currently show moderately high lithium-ion (Li^+) conductivities on the order of 10^{-6} to $10^{-3} \text{ S cm}^{-1}$ at

room temperature.^[1] Thiophosphates, such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) with $12\times 10^{-3} \text{ S cm}^{-1}$ and $\text{Li}_2\text{S-P}_2\text{S}_5$ (LPS) with $17\times 10^{-3} \text{ S cm}^{-1}$, have recently emerged as a promising alternative with conductivities at room temperature comparable to organic liquid electrolytes.^[2] Despite the high bulk conductivity of thiophosphates, their limited chemical and electrochemical interface stability with anode and cathode active materials has hindered their integration into competitive batteries.^[3]

Li^+ conduction was also discovered in complex hydrides, which have been studied extensively as potential hydrogen storage materials.^[4] As SSEs for lithium-ion batteries, they offer multiple advantages including the natural abundance of their constituent elements, their light weight, negligible electronic conduction, and low grain boundary resistance.^[5] The prototypical example is LiBH_4 , whose Li^+ conductivity increases abruptly to $>1\times 10^{-3} \text{ S cm}^{-1}$ above 100°C due to a structural phase transition.^[6] This superionic high temperature phase can be stabilized at room temperature by incorporation of lithium halides ($\text{LiBH}_4\text{-LiX}$, $\text{X}=\text{Cl}$, Br , I). Among these materials, the solid solution with lithium iodide displays the highest conductivity at room temperature of $>10^{-5} \text{ S cm}^{-1}$.^[7] Conductivities reaching $10^{-4} \text{ S cm}^{-1}$ near room temperature have also been reported for two compounds of the lithium amide-borohydride $\text{Li}(\text{BH}_4)_{1-x}(\text{NH}_2)_x$ system, namely for the cubic α phase ($x=3/4$) and for the trigonal β phase ($x=1/2$).^[4, 8]

Here, we report the discovery of a transition to even higher Li^+ conductivities of up to $6.4\times 10^{-3} \text{ S cm}^{-1}$ near room temperature (40°C) in BH_4 -rich lithium amide-borohydride ($x=2/3$). We discuss the conduction mechanism in light of latent heat absorbed/released during the transition upon heating/cooling, respectively. We further demonstrate an all-solid-state $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based half-cell (employing the BH_4 -rich electrolyte) with excellent rate capability and cycling stability, comparable to a reference cell with standard liquid electrolyte representing an important step towards an all-solid-state amide-borohydride-based battery.

2. Results and Discussion

$\text{Li}(\text{BH}_4)_{1-x}(\text{NH}_2)_x$ powders, employing LiBH_4 and LiNH_2 precursors in amounts equivalent to $x=2/3$, were prepared via reactive ball milling for 45 min and subsequent heat treatment at 120 °C for 12 h (see Experimental Section for details). A reference sample with $x=3/4$ (cubic α phase) and intermediate compositions were also synthesized.

Ionic conductivities were determined for pellets pressed from the powders via temperature-dependent impedance spectroscopy. For low to intermediate conductivities, Nyquist plots take the typical form composed of a single semicircle and the electrode polarization tail (see **Figure S1** for exemplary Nyquist plots). Conductivities as a function of temperature extracted from the intercept of impedance with the horizontal axis of the Nyquist plots are shown in **Figure 1a** for both heating and cooling cycles. The data shows thermal hysteresis between heating and cooling, also observed in other complex hydrides.^[6, 9]

For the reference sample $x=3/4$, our measurements reproduce a conductivity of $2 \times 10^{-4} \text{ S cm}^{-1}$ at 40 °C with an activation energy of 0.34 eV in agreement with previous reports.^[8a] We find that the conductivity can be improved by more than one order of magnitude to $6.4 \times 10^{-3} \text{ S cm}^{-1}$ by increasing the precursor ratio $\text{LiBH}_4:\text{LiNH}_2$ to 1:2 ($x=2/3$). These conductivity values are remarkably five and seven orders of magnitude higher than the conductivities of the individual constituent compounds LiBH_4 and LiNH_2 , respectively, also shown in Figure 1a. The activation energy of 0.30 eV above 40 °C is comparable to the activation energy of the reference. Below 40 °C, the slope steepens abruptly indicating a transition, whose nature will be discussed below. Conductivities for intermediate compositions fall close to a straight line as a function of composition x (see **Figure S2**).

To put our results into perspective, a plot of conductivity vs. activation energy is presented in Figure 1b showing the data for our amide-borohydrides at 40 °C (red points),

1 along with the respective values of oxide, thiophosphate, and complex hydride SSEs (see
2 **Table S1 to S3** for tabulated data). Our highest conducting amide-borohydride is among the
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4 SSEs that exhibit conductivities exceeding that of liquid electrolytes typically used for
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6 lithium-ion batteries (e.g., 1M LiPF₆ in a 1:1 volumetric mixture of ethylene carbonate (EC)
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8 and ethyl methyl carbonate (EMC)). Higher conductivities have only been reported for several
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10 thiophosphates and recently for a monocarba-*closo*-borate solid solution also indicated in
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12 Figure 1b.^[2a, 3e, 10]
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17 X-ray diffraction (XRD) patterns measured between 30 and 100 °C for the $x=2/3$ high
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19 conductivity sample and the $x=3/4$ reference sample are shown in **Figure 2a** and b. The XRD
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21 pattern for the $x=3/4$ reference sample matches the pattern of the cubic α phase reported in
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23 literature.^[11] For $x=2/3$, the dominant reflections are very similar, showing that the cubic α
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25 phase is preserved. The lattice parameter is slightly larger than for the $x=3/4$ phase (10.670 vs.
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27 10.655 Å), indicative of a solid solution in which NH₂⁻ units are replaced by larger BH₄⁻ units.
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29 No sign of a structural phase transition at 40 °C is observed for the $x=2/3$ phase and the
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31 refined lattice parameters as function of temperature show only slight thermal expansion, see
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33 **Figure S3**. Additional weak reflections that disappear at 40 °C, marked by a star in Figure 2a,
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35 indicate the presence of a second phase resembling the previously described meta-stable γ
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37 phase within the amide-borohydride phase diagram.^[12] Intermediate compositions show
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39 decreasing intensities of minor phase reflections with decreasing BH₄ content (**Figure S4**).
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47 The crystal structure of the α phase is shown in Figure 2c. Li(BH₄)_{1/4}(NH₂)_{3/4}
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49 crystallizes in the cubic lattice system with space group $I2_13$ with three inequivalent lithium
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51 sites (Figure 2e) tetrahedrally coordinated by a combination of BH₄⁻ and NH₂⁻ anions (blue
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53 tetrahedra).^[11] The structure contains a second set of tetrahedra, of equal number, which
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55 remain empty to guarantee charge neutrality (yellow tetrahedra). Empty sites facilitate the
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57 migration of Li-ions. Filled and empty tetrahedra form symmetry-related dual sublattices as
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can be seen from comparison of Figure 2c and d. Both sublattices form percolating, interpenetrating networks. The two structures previously reported in literature for the cubic α phase are related by a screw transformation.^[11, 13] As a consequence of the cation-anion electrostatic attraction, the occupied tetrahedra are contracted in comparison to the empty ones.

We examined the energy barriers for lithium hopping in the cubic α phase within density functional theory using the climbing-image nudged elastic band method. While the calculated values of the individual energy barriers depend on the exact lithium configuration, we can divide all considered lithium hopping processes into two categories, (1) hopping events from the filled sublattice into the empty sublattice and (2) hopping events within the empty sublattice. Results for representative events are shown in **Figure 3a** and b. As can be seen from Figure 3a, activation of lithium from the filled sublattice into the empty sublattice faces a large energy barrier of more than 1 eV, a consequence of the tetrahedra contraction. This energy barrier is too high for thermal activation of lithium into the empty sublattice. However, some lithium is expected to occupy the empty sublattice as a result of structural defects and small grain size. In contrast, as shown in Figure 3b, hopping events within the empty sublattice must overcome much lower energy barriers on the order of only 0.3-0.4 eV, a value in excellent agreement with the activation energy extracted from the conductivity data in Figure 1a. Note that the energies of sites B and C are not identical, due to the inequivalency of these two lithium sites.

It has been shown earlier in the context of sulfur-based SSEs that Li-ion hopping between face-sharing tetrahedral sites occurring in body-centered cubic (bcc) lattices requires the least amount of energy. In face-centered cubic (fcc) lattices, where only edge- and corner-sharing tetrahedra exist, Li-ions follow an energetically more expensive path through an intermediate octahedrally coordinated site.^[14] The cubic α phase of lithium amide-

borohydrides can be mapped onto a distorted fcc lattice as shown in Figure 3c and d. Migration between two corner-sharing tetrahedral sites in Figure 3c proceeds also through an intermediate octahedrally coordinated site, resulting in a high energy barrier (see again Figure 3a). Compared to the single-atom anion fcc framework discussed in ref. ^[14], hopping between two edge-sharing tetrahedral sites within the same sublattice of α phase lithium amide-borohydride is energetically more favorable due to reorientation of the anions, especially of polar NH_2^- (see arrows in Figure 3d). This lowers the energy barrier significantly (compare Figure 3b) and enables efficient lithium migration in the cubic α phase.

We also investigated variations of the α phase, in which NH_2^- anions are replaced by BH_4^- anions, preserving the symmetry of the unit cell, in order to simulate phases with $x < 3/4$. We find that the activation energy for transferring Li between the occupied and empty sublattices is lowered by around 20% when increasing the BH_4 content from $x = 3/4$ towards $x = 2/3$, while the energy barriers for Li hopping within the empty sublattice remain almost unaffected by the change in stoichiometry in the range $2/3 \leq x \leq 3/4$. However, the energy barrier to excite Li into the empty sublattice is still too high to account for the high conductivity observed for $x = 2/3$. In addition, such a conduction mechanism does not predict the observed transition to high conductivity near 40 °C.

Additional insights into the origin of the high conductivity can be obtained from differential scanning calorimetry shown in **Figure 4a** for both $x = 3/4$ and $x = 2/3$. A pronounced endothermic/exothermic event is observed near 40 °C for the highly conducting $x = 2/3$ sample upon heating/cooling respectively. As in the conductivity data, we observe a marked thermal hysteresis. The onset temperatures coincide roughly with the temperatures at which the slope of the conductivity in Figure 1a changes abruptly. The latent heat ΔH at the transition is 40 J g⁻¹, which corresponds to an entropy change ΔS of 0.13 J g⁻¹ K⁻¹ (at the transition $\Delta G = \Delta H - \Delta S \cdot T = 0$). A significantly smaller event with $\Delta H = 2.2$ J g⁻¹ is also observed for the reference ($x = 3/4$), which we attribute to a slight deviation from perfect stoichiometry. In fact, as can be

seen from the inset of Figure 4a, ΔS decreases monotonically with composition x and vanishes at $x=3/4$ (see **Figure S5** for DSC data).

Latent heat and hysteresis are indicative of a first order phase transition. From the XRD data in Figure 2a, we know that the bulk of the sample remains in the crystalline α phase. Ref. ^[15] discusses a sublattice melting scenario in the context of lithium amide-borohydrides, in which the filled lithium sublattice in the cubic α phase undergoes a sublattice melting transition, whereby lithium overcomes the barrier between occupied and empty sublattices and populates both sublattices with comparable probability. However, according to the Clausius-Clapeyron relation, the absorption of latent heat is accompanied by a finite volume change, which is not observed in our case, judging from the smooth increase of the lattice parameter with increasing temperature in Figure S3.

Latent heat could also be associated with a transition of a side phase coexisting with the α phase. Indeed, the XRD pattern displayed in Figure 2a contains a series of low intensity reflections (marked by a star) which disappear at 40 °C. A similar observation has been made in ref. ^[12]. The increase of latent heat with increasing BH_4 content indicates an increasing fraction of side phase in BH_4 -rich samples in line with XRD (see again Figure S4 and S5). From the phase diagram in ref. ^[16] and our nominal composition, we estimate that the side phase contains 25% of the lithium. Importantly, above the transition, the anions stay intact as H_2 or NH_3 gas release is observed only above 250 °C in thermogravimetry coupled with mass spectrometry.^[12] The transition may lead to the formation of a disordered, highly conducting state consisting of Li^+ cations and NH_2^- and BH_4^- anions coexisting with the α phase, with no long range coherence, explaining the weak signal in XRD below the transition.

To further investigate the origin of the high Li-ion conductivity, temperature-dependent nuclear magnetic resonance (NMR) measurements on the ^7Li and ^1H nuclei, a bulk technique that integrates over the entire sample, were carried out (see **Figure S6 and S7**). We

observe no change in shape and only a slight reduction in the line widths of the ^7Li signal between 25 and 70 °C for the reference sample ($x=3/4$). In contrast, an additional much sharper component develops above 40 °C for the highly conducting $x=2/3$ sample resulting in an overall abrupt line width reduction (Figure 4b). We attribute this to motional narrowing of Li-ions in the disordered side phase. By deconvolution of the ^7Li NMR spectrum into two components (Figure S8), we estimate that the fraction of mobile Li^+ above the transition is about 30%, a value that compares well to the 25% of Li contained in the side phase estimated above. Concomitant line width narrowing is observed for the ^1H signal (Figure 4c), indicative of enhanced anion dynamics and strong lithium-anion coupling.

To investigate whether the high AC conductivity of the $x=2/3$ sample can translate to fast DC Li^+ transport in a lithium-ion battery, we assembled a quasi-symmetric all-solid-state half-cell with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as working electrode, the $x=2/3$ sample as SSE, and a pre-lithiated oversized LTO counter electrode. We chose LTO as active material because its lithiation/delithiation potential (~ 1.55 V vs. Li/Li^+)^[17] lies conveniently in the stable potential range of our SSE (0.7 – 2.0 V vs. Li/Li^+ , Figure S9). LTO further shows fast lithiation and delithiation kinetics, minimizing capacity fading unrelated to the SSE at high current densities. The half-cell was cycled at different current loads at 40 °C and compared to a reference cell using a typical liquid electrolyte. Results are shown in Figure 5a.

The two cells show nearly identical capacities at rates of 0.1 to 0.5C. At higher rates, the SSE cell delivers slightly lower capacities than the cell with the liquid electrolyte, which is possibly owing to a smaller contact area between LTO and SSE in the composite electrodes of the all-solid-state cell. Nevertheless, the LTO electrode paired with the SSE also demonstrates good performance at a rather high current density of 3.5 mA cm^{-2} (5C) with a capacity of 101 mAh g^{-1} , proving fast DC Li^+ transport through the bulk of the SSE and across the LTO particle–SSE interfaces. The SSE pellet used for this cell had a thickness of ca.

1 mm. Even better performance can be expected by reducing the thickness of the SSE layer. Coulombic efficiencies, also shown in Figure 5a, at all tested current rates approach 100%.

The high stability of both the SSE–LTO interface and the Li^+ conduction within the SSE is further demonstrated by the stable capacity and Coulombic efficiency of this cell upon continued cycling at 1C to at least 400 cycles (Figure 5b).

3. Conclusions

The high ionic conductivity, high interfacial stability in contact with LTO, excellent rate and stable long term cycling capability demonstrated in this work render lithium amide-borohydride electrolytes promising candidates for the realization of a competitive all-solid-state lithium-ion battery. The high ionic conductivity is realized in BH_4 -rich $\text{Li}(\text{BH}_4)_{1-x}(\text{NH}_2)_x$ compounds where the presence of additional BH_4^- within the cubic α phase and/or the presence of a disordered side phase enables fast Li-ion diffusion. However, the limited oxidative stability requires the use of protective coatings on the cathode side to realize a high-voltage battery. Understanding how to design such interfacial layers may be the key to widening the operative voltage window and consequently increase the energy density of all-solid-state batteries.^[18]

Experimental Section

Synthesis: LiBH_4 (purity: 95%) and LiNH_2 (purity: 95%) were purchased from Alfa Aesar. $\text{Li}(\text{BH}_4)_{1-x}(\text{NH}_2)_x$ samples with nominal compositions $x=0.667$, 0.722, 0.737 and 0.750 were prepared from stoichiometric mixtures of LiBH_4 and LiNH_2 by high-energy ball milling for 45 min using a SPEX 8000M mill and a balls-to-sample mass ratio of 10 to 1. After ball milling, a heat-treatment was carried out under hydrogen atmosphere (ca. 100 bar) at 120 °C for 12 h. Samples were handled in an argon-filled glovebox to avoid air exposure.

Characterization: XRD measurements were performed on a Bruker D8 diffractometer equipped with a Goebel mirror selecting Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a linear detector system (Vantec) using sample powders sealed in glass capillaries under argon atmosphere. Structural representations were prepared with the visualization program VESTA Version 3.^[19] Differential scanning calorimetry (DSC) was conducted using a TA Instruments Q2000 with Al sample pans under an Ar flow of 50 ml min^{-1} . Heating/cooling rates were $5 \text{ }^{\circ}\text{C min}^{-1}$ and samples were cycled between -20 and $70 \text{ }^{\circ}\text{C}$. Temperature-dependent static solid-state NMR experiments were performed on a Bruker Advance III 400 MHz NMR spectrometer using a 4 mm cross polarization magic angle spinning probe. ^7Li and ^1H NMR spectra were recorded at 155.5 and 400.2 MHz, respectively. The samples were equilibrated for 10 min at each temperature. Ionic conductivity was measured by alternating current (AC) impedance spectroscopy using a Zahner IM6ex electrochemical workstation in 2-electrode stainless steel cells. The frequency was varied between 3 MHz and 10 Hz. Molybdenum (Mo) blocks were used as electrodes. All powder samples were pressed into pellets with a diameter of 12 mm and a thickness of ca. 1.6 mm under a pressure of 0.9 GPa. The $\text{Mo/Li(BH}_4\text{)}_{1-x}\text{(NH}_2\text{)}_x\text{/Mo}$ cells were pre-treated at $70 \text{ }^{\circ}\text{C}$ for 2 h before the impedance measurements and thermally equilibrated for 2 h at each temperature.

Cell tests: The electrochemical stability window of $\text{Li(BH}_4\text{)}_{1-x}\text{(NH}_2\text{)}_x$ with $x=2/3$ was determined via linear sweep voltammetry with a scan rate of $100 \text{ } \mu\text{V s}^{-1}$ in 3-electrode Swagelok cells at $40 \text{ }^{\circ}\text{C}$ using a Pt working electrode and lithium counter and reference electrodes. Separate cells were used to determine the anodic and cathodic stability limits. The electrolyte was also electrochemically tested in half-cell configuration in combination with a lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) anode. An oversized LTO counter electrode served as lithium reservoir. The tests were carried out in 3-electrode Swagelok cells at $40 \text{ }^{\circ}\text{C}$. A mixture of LTO ($<200 \text{ nm}$ particle size, purity: $>99\%$, Sigma-Aldrich), carbon black (C-ENERGYTM

SUPER C65, IMERYS Graphite & Carbon) and SSE in a mass ratio of 45:20:35 was prepared by grinding the three components for 15 min under protective argon atmosphere in a glovebox. Three-layer pellets consisting of 10 mg of the LTO mixture as the working electrode, 80 mg SSE as the electrolyte layer and 25 mg of the LTO mixture as the counter electrode were prepared by compacting the components in a mold with a diameter of 12 mm using a hydraulic press (15 t, 1 min). The thickness of the resulting pellet was ca. 1 mm. A piece of lithium serving as reference electrode was brought into contact with the edge of the LTO/SSE/LTO pellet via a small connecting piece of solid-state electrolyte. The oversized LTO counter electrode was electrochemically pre-lithiated at low rates (typically C/400) to about 50% state-of-charge through the lithium reference electrode to introduce sufficient lithium into the system. A rate test was carried out in the potential range of 1.0 to 2.0 V vs. Li/Li^+ with current rates ranging from C/10 to 5C corresponding to current densities between $70 \mu\text{A cm}^{-2}$ and 3.5 mA cm^{-2} . For comparison, the same rate test was carried out for a reference cell with liquid 1M LiPF_6 in EC:EMC 1:1 (v:v) (battery grade, Sigma-Aldrich) as the electrolyte. The cycle life of the SSE cell was investigated by subjecting it to prolonged cycling at 1C after the rate test.

Calculations: Density functional theory with the Perdew-Burke-Ernzerhof generalized gradient approximation for the exchange correlation functional was used.^[20] The core/valence electrons interaction is described by the projector augmented wave method as implemented in the VASP package.^[21] The pseudopotentials $1s^2 2s^1$ for Li, $2s^2 2p^1$ for B, $2s^2 2p^3$ for N, and $1s^1$ for H were used. Activation energy barriers for Li^+ hopping were calculated within the climbing-image nudged elastic band method in a conventional unit cell.^[22] A kinetic energy cutoff of 500 eV was used for energy barrier calculations. For the initial and final states, atomic configurations were optimized with fixed unit cell parameters, and each barrier was calculated with a combination of steepest descent and conjugated gradient algorithms. Due to

significant relaxation of the atomic positions and molecular orientations related to Li^+
migration at least three independent calculations were performed for each pathway.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. a) Arrhenius plots of the ionic conductivity for $\text{Li}(\text{BH}_4)_{1-x}(\text{NH}_2)_x$ with $x=2/3$ (in red) and $3/4$ (in black), and of the precursors LiBH_4 and LiNH_2 . Open symbols denote heating runs; filled symbols, cooling runs. b) Li-ion conductivity vs. activation energy for $\text{Li}(\text{BH}_4)_{1-x}(\text{NH}_2)_x$ at 40 °C (red dots) with values of other lithium solid-state electrolytes reported in literature. The number next to the arrows indicates the composition x . For more information on the individual compounds see Table S1 to S3. The dashed line represents the estimated Li-ion conductivity of the liquid electrolyte 1M LiPF_6 in EC:EMC 1:1 (v:v) ($4.5 \times 10^{-3} \text{ S cm}^{-1}$, after considering a lithium transference number of 0.35).

Figure 2. XRD patterns vs. temperature for $\text{Li}(\text{BH}_4)_{1-x}(\text{NH}_2)_x$ with a) $x=2/3$ and b) $x=3/4$. c) Polyhedral representation of the crystal structure of the cubic α phase for $x=3/4$ and d) its symmetry-related dual structure along with e) the three inequivalent lithium sites occurring in the structure. Anion tetrahedra filled with lithium (empty) are shown in blue (yellow). Li, B and N atoms are colored red, green and grey, respectively. H atoms are only shown in e) for clarity.

Figure 3. Calculated energy along lithium migration paths in $\text{Li}(\text{BH}_4)_{1-x}(\text{NH}_2)_x$ ($x=3/4$) including a) the excitation of a Li-ion from the occupied sublattice (position A) into a neighboring site of the originally empty sublattice (position B) and b) lithium migration within the originally empty sublattice (migration from position B to C). Crystal structures illustrating the starting and final lithium sites are also shown. c,d) Lithium migration paths corresponding to a) and b), respectively. The rotation of the NH_2^- anion is indicated by arrows. The intermediate octahedral site employed in transition c) is shown in red.

Figure 4. a) Differential scanning calorimetry profiles for compositions $x=2/3$ (red) and $3/4$ (in black) measured at a rate of 5 K min⁻¹. The inset shows the correlation between composition x and the entropy change ΔS at the transition. Temperature-dependent full widths at half maximum (FWHM) of b) ⁷Li and c) ¹H static solid-state NMR signals for compositions $x=2/3$ and $3/4$.

Figure 5. LTO half-cell tests at 40 °C using $\text{Li}(\text{BH}_4)_{1-x}(\text{NH}_2)_x$ ($x=2/3$) as the electrolyte. a) Comparison of discharge capacities and Coulombic efficiencies at different rates for two LTO half-cells with solid-state electrolyte (SSE) and liquid electrolyte 1M LiPF_6 in EC:EMC 1:1 (v:v) (LP50). The current density of 3.5 mA cm^{-2} (5C, i.e. 875.5 mA g^{-1}) is approximately equivalent to that needed to charge/discharge a commercial lithium-ion battery in 1 h. b) Constant current cycling of the SSE cell at 1C, carried out after the rate test.